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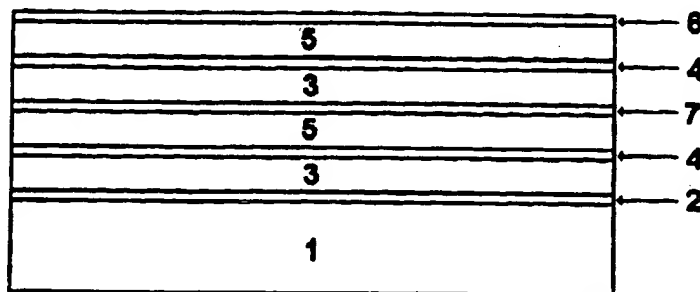
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(54) Title: A SOLID STATE BATTERY USING AN IONIC OR PROTONIC ELECTROLYTE



## (57) Abstract

A solid state battery comprising a substrate (1); at least one multilayered electrochemical cell deposited onto the substrate (1), the multilayered electrochemical cell comprising: a layer of negative electrode material (3) capable of electrochemically adsorbing and desorbing ions during charge and discharge; a layer of positive electrode material (5) capable of electrochemically desorbing and adsorbing ions during charge and discharge; and a layer of insulating/conducting material (4) disposed between the layer of positive electrode material (5) and the layer of negative electrode material (3), where the layer of insulating/conducting material (4) is electrically insulating and capable of readily conducting or transporting ions from the layer of positive electrode material (5) to the layer of negative electrode material (3) while the battery is charging and from the layer of negative electrode material (3) to the layer of positive electrode material (5) while the battery is discharging; and an electrically conductive layer (6) deposited atop the last of the at least one multilayered electrochemical cells, the electrically conductive layer (6) providing one battery terminal.

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**A SOLID STATE BATTERY  
USING AN IONIC OR PROTONIC ELECTROLYTE**

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**FIELD OF THE INVENTION**

The present invention relates generally to solid state ionic conductors and more specifically to electrically insulating ionic conductors useful as solid state electrolyte and thin-film all solid state batteries employing these ionic conductors.

**BACKGROUND OF THE INVENTION**

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Rechargeable batteries are used in almost every aspect of daily life. A wide variety of industrial, commercial and consumer applications exist. Larger capacity battery uses include such applications as fork lifts, golf carts, uninterruptable power supplies for protection of electronic data storage, and even energy storage for power production facilities. When electric vehicles are manufactured in mass, demand for low weight, high charge capacity batteries will be greater than ever before. Indeed, to make mass use of electric vehicles economically feasible, very high specific capacity may be critically necessary.

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In electric vehicles, weight is a significant factor. Because a large component of the total weight of the vehicle is the weight of the batteries, reducing the weight of the cells is a significant consideration in designing batteries to power electric vehicles.

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The 1998 California Clean Air Act has posed an exceptional challenge on battery scientists and engineers to develop an improved battery that can support the commercialization of electric vehicles (EV). Needless to say, the law has not changed the reality of battery technology. In over 100 years of rechargeable battery usage, two chemistries namely: Pb-PbO<sub>2</sub> (known as lead-acid battery) and Cd-NiOOH (known as Ni-Cd battery) have dominated with more than 90% of the market. Neither of the two are likely to fulfill the utopian goals of powering an electric car that will match the range, economy, and performance of an internal combustion engine vehicle. Therefore, battery scientists and engineers are forced to study new battery chemistries.

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In addition to industrial, commercial and other large scale uses of batteries, there are literally thousands of consumer applications of rechargeable batteries. A rechargeable electrochemical cell is ideally suited to serve as a portable power source due to its small size, light weight, high power capacity and long operating life. A rechargeable cell may operate as an "install and forget" power source. With the exception of periodic charging, such a rechargeable cell typically performs without attention and rarely becomes the limiting factor in the life of the device it powers.

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Present rechargeable battery systems can be classified into two groups those

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employing liquid electrolytes and those employing solid electrolytes. Liquid electrolyte systems have been around for many decades and are the most well known to the general public. Examples of liquid electrolyte rechargeable battery systems include lead-acid, nickel cadmium, and the more recent nickel-metal hydride systems.

5 A more recent advancement is the solid electrolyte rechargeable battery systems. The solid electrolyte devices have several distinct advantages over those based on liquid electrolytes. These include (1) the capability of pressure-packaging or hard encapsulation to yield extremely rugged assemblies, (2) the extension of the operating temperature range since the freezing and/or boiling-off of the liquid phase, which drastically affect the device  
10 performance when employing liquid electrolytes are no longer a consideration, (3) solid electrolyte devices are truly leak-proof, (4) they have long shelf life due to the prevention of the corrosion of electrodes and of loss of solvent by drying out which occur when using liquid electrolytes, (5) solid electrolytes permit micro-miniaturization, and (6) they do not require heavy, rigid battery cases which are essentially "dead weight" because they provide no additional  
15 capacity to the battery but must be included in the total weight thereof.

All of the above considerations have led to a growing use of solid electrolytes. Solid state batteries and timers are already available which employ the solid electrolyte as a cylindrical pellet with suitable electrodes on either side. However, this kind of geometry leads to somewhat poor solid-solid contacts and these devices tend to have high internal resistances  
20 and polarization losses. These problems have been overcome by the use of thin films as the electrolytes, since thin films deposited on top of each other have excellent contacts and should also be able to withstand shocks, acceleration forces and spin rates without undue damage.

In forming such a battery system, a solid ion conductor (i.e. solid electrolyte) for moving ions within the system is required. A solid electrolyte is classified by its type of  
25 movable ion, such as  $\text{Li}^+$ -conductive solid electrolyte,  $\text{Ag}^+$ -conductive solid electrolyte,  $\text{Cu}^+$ -conductive solid electrolyte,  $\text{H}^+$ -conductive solid electrolyte, etc. A solid electrochemical element is constituted by combining one of these solid electrolytes with an appropriate electrode material. Several solid electrolytes are known to exhibit good ionic conductivity, some of which exist in the form of thin films. Oxide ion conductors such as zirconia are operated at  
30 high temperatures due to their low conductivity at ambient temperatures. Chloride ion conductors such as  $\text{PbCl}_2$  and  $\text{BaCl}_2$  have similar temperature restrictions. Silver ion such as  $\text{AgBr}$ ,  $\text{AgCl}$ , and  $\text{AgI}$  also show low room temperature ionic conductivity.

Of the thin-film, solid state battery systems, lithium-polymer batteries have received the most widespread interest. Reports in 1979 that lithiated poly-ethylene-oxide (PEO) possesses  
35 lithium ion conductivity raised the expectations for a solid state battery employing PEO as solid electrolyte. Indeed, if PEO, or other polymers, were a true solid electrolyte with practical ionic conductivities and a cationic transfer number of 1, a stable interface with the lithium electrode

and good charging uniformity could be realized. The expectations, no doubt, were stimulated by the relative success of the true solid electrolyte "B" Alumina, in the Sodium Sulphur battery.

More recently, several researchers proposed the use of "plasticized polymers" to enhance conductivity at room temperature. Although the term "plasticized polymers" is the correct material science terminology for the materials, they are in effect no different than a battery separator filled with organic solvent and electrolyte. In this case, we are back to liquid filled systems with all the old unsolved fundamental problems and several new ones.

Solid electrolytes consist of solid atomic structures which selectively conduct a specific ion through a network of sites in a two or three dimensional matrix. If the activation energy for mobility is sufficiently low, the solid electrolyte can serve as both the separator and electrolyte in a battery. This can allow one to fabricate an all solid state cell.

An important aspect of such electrolytes is that they selectively conduct only one type of ion. If that ion features reversible electrochemistry with both the positive and negative electrode of the battery, and if the solid electrolyte itself is inert to the electrodes, the cell will enjoy a uniform and reversible electrochemistry with no composition change and no passivation or side reactions.

While true solid electrolyte lithium conductors would not exhibit the inherent problems of Li-polymer systems described herein below, all polymer electrolytes reported to date are not true solid electrolytes. The conductivity occurs in an amorphous zone that conducts anions better than it conducts lithium ions (the transfer number of lithium is less than 0.5). As such, ion concentrations in the electrode surface are variable and irreversible reactions between the anion and the lithium electrodes do occur. The combination of the two effects brings about partial passivation of the lithium surface with non uniform dendritic plating on charge. Additionally, the conductivity of the polymer electrolyte is too low, typically two to four orders of magnitude lower than that of aqueous electrolyte. Also, the electrode area required for a 20 kwh battery is 42 m<sup>2</sup> for Ni-Cd batteries and is 1610 m<sup>2</sup> for Li-Polymer batteries. This data clearly conveys that in order to deliver acceptable power levels for EV applications, lithium polymer batteries will require nearly two orders of magnitude, larger electrode area per ampere hour than a higher power density Ni-Cd battery. Given that electrode processing is the most expensive component in battery production and that the cost of electrode processing is nearly linear with electrode area, the cost implications of the design are astonishing.

In addition to cost, safety of Li batteries, particularly liquid electrolyte systems, is always a problem. The single most important reason rechargeable lithium batteries have not been successful in the market place is their poor safety record. Most research groups that have worked on rechargeable lithium cells have "personally experienced" explosions, and explosions have occurred in the field. The problem can be diagnosed as follows: 1) lithium plating is dendritic, 2) dendrites eventually short through the separator, 3) shorted cells heat up during

charging, 4) shorted cells will go into reversal during full battery discharge, 5) low capacity cells will go into reversal during full battery discharge, 6) in reversal, lithium is likely to plate on the cathode which can cause direct chemical reaction between cathode material and lithium, 7) processes 3 and 6 can generate enough heat to melt lithium (165 Centigrade), and 8) molten lithium is an extremely strong reducing agent which will react with most organic and inorganic materials. An explosion could occur depending on: (a) the amount of lithium in the cell, (b) the surface to volume aspect ratio of the cell, (c) the reactivity of the other cell components to lithium, (d) the vapor pressure of the products, and (e) the vent design.

Battery design should be aimed at minimizing the risk of lithium melt down. Given that it is extremely unlikely that lithium melt down can be completely avoided in mass usage of large rechargeable lithium batteries, it is essential to guarantee non explosion when the melt down does occur. Dry polymer electrolyte offers some improvement with regard to exposition when compared to high vapor pressure liquid electrolyte. However, that improvement is counteracted by the need for a very thin separator. Overall, the likelihood of ensuring explosion free melt downs in large cells and batteries is diminutive.

Cells utilizing polymer electrolytes that contain organic solvents, are as likely to be explosive as cells with standard (polymeric) separator and liquid electrolytes. In this case, depending on cell design, common experience places the explosion threshold in the 0.5 to 5 Ah size range; two orders of magnitude smaller than what is required for an EV battery. It should be noted that a cycled lithium electrode is more prone to explosion than a fresh uncycled one. While this fact has been known for quite some time, lithium polymer battery developers have shied away from publishing safety test data on cycled cells.

In spite of its safety problems, there is a continued interest in lithium batteries because of their purportedly high power density. This feature makes rechargeable lithium batteries attractive. Theoretical energy densities of most rechargeable lithium chemistries are two and a half to three times higher than that of Pb-Acid and Ni-Cd batteries. Indeed, liquid electrolyte rechargeable lithium batteries could be made to deliver up to 150 Wh/Kg and 200 Wh/liter. This is about three times higher than the practical gravimetric energy density delivered by the best Ni-Cd batteries and four times higher than the practical gravimetric energy density delivered by the best Pb-Acid batteries. However, the design of the lithium polymer batteries, driven by the poor conductivity of the polymer electrolyte, is very volume inefficient. Specifically, the separator occupies 30% of the stack volume, carbon is added to the positive electrode in concentration of up to 30% and the positive electrode utilization is poor. Thus, the practical energy density is likely to be considerably lower than of what can be achieved with liquid electrolyte. Estimated deliverable energy density of lithium polymer batteries is 15-20% of the theoretical energy density. This translates to (using 485 Wh/Kg as theoretical maximum) approximately 70 to 100 Wh/Kg at best. Most likely, compromises that will have to be made

to improve manufacturability, safety and cycle life beyond the current laboratory state-of-the-art technology. This will have the effect to reduce the practical energy density to even below the values proposed above. The power capability of a battery depends upon the physical and chemical properties of the cell components as well as the cell design. Lithium polymer battery developers are trying to counteract the poor inherent conductivity of the polymer electrolytes by reducing the electrode and separator thickness. Because practical manufacturing reality is likely to impose increases in the electrolyte thickness from approximately 2 to 4 mil, the power deliverable by the cell is likely to drop by 30 to 50%.

An area that requires closer attention is power degradation over life. The main degradation mechanism of the cell involves irreversible reactions between lithium and electrolyte. This reduces the conductivity of the electrolyte as well as increases the impedance of the Lithium electrode due to the formation of passive films; both effects reduce the deliverable power from the battery. Because the cycle life of the lithium polymer battery is short, significant degradation in power is likely to occur in less than 100 cycles.

Other problems arise from real life usage and requirements placed upon battery systems. Traction batteries are assembled from a string of individual cells connected in series. During both charge and discharge, the same amount of current will pass through all the cells. In practical manufacturing and usage, it is impossible to keep all cells at exactly the same state of charge. This forces a weak cell in a battery to go into reverse during deep discharge and some cells to go into overcharge during full charge. For a battery to operate at deep discharge cycles, it is essential that individual cells tolerate reverse or overcharge without damage or safety implications.

Lithium batteries are very poor in this respect. Over discharge will result in plating lithium on the positive electrode which can result in a spontaneous chemical reaction with severe safety implications. Overcharge is likely to result in electrolyte degradation that can generate some volatile gasses as well as increase cell impedance. These problems are particularly severe for lithium cells because: 1) degradation occurs during cycle life, therefore, even if initial capacities are matched very closely, it is unreasonable to expect that the degradation rate will be identical for all cells, 2) the cells tend to develop soft or hard shorts, thereby making it impossible to maintain the cells at the same state of charge at all times, and 3) cell capacity is dependent on temperature, therefore cells that are physically cooler due to their location will deliver less capacity than others. These conditions make the likelihood of cell reversal, relatively early in the life of the battery, very high. Of course, cell reversal is likely to result in venting and or explosion.

It has been propose to install individual diode protection for all cells which could be an expensive, although practical, solution for a portable low watt-hour battery. The increased cost and reduced reliability associated with this solution makes this very undesirable for an EV



battery. Plus, the inherent lack of overcharge and over discharge capability eliminates any possibility of ever developing a rechargeable lithium-polymer battery of a bipolar design.

5 An additional problem with the commercialization of Li-polymer batteries is their high cost. It is difficult to assess the cost, although clearly, processing cost per watt-hour should be much higher than that of traditional batteries. Raw material costs are clearly higher than Pb-Acid, although, it may be similar to Ni-Cd. The cost of raw material will rise due to high  
10 purity requirements. There are convincing reasons to expect that lithium polymer batteries, if ever made commercially, will be considerably more expensive than Ni-Cd batteries considering that: 1) primary Li-MnO<sub>2</sub> cells, which are in mass production, are still more expensive than Ni-Cd cells, 2) the purity requirements for a secondary cell are much higher than that of a primary cell, and 3) the electrode area per watt-hour of a lithium polymer secondary battery will be approximately an order of magnitude larger than that of a primary Li-MnO<sub>2</sub> battery.

15 Even more problematic than the cost factor is the low cycle life of the lithium polymer batteries, which is particularly important in EV applications. Small rechargeable lithium batteries employing organic liquid electrolyte have delivered 100 to 400 cycles in laboratory tests. It is anticipated that lithium polymer electrolyte batteries of the same size could be made to deliver a comparable number of cycles. However, all the data published to date on lithium polymer batteries was run on cells with a very large amount of excess lithium, therefore, no conclusion can be drawn at this stage.

20 The cycle life of a large multi cell battery is likely to be considerably lower than that of a small two-cell battery. Additional reduction of the expected cycle life results from consideration of the fact that the battery will be limited by the weakest cell, and as previously mentioned, the likelihood of temperature or electrical imbalance is high. Further, power may degrade faster than capacity, so cycle life could become limited due to an unacceptable drop  
25 in power. Therefore, it is probably a fair assumption that if a full size battery was built at today's state-of-the-art technology, it could possibly make 100 cycles or so, which is about an order of magnitude short of what is required for an EV.

30 Therefore, since lithium-polymer batteries will be inadequate to meet today's requirements for a universally acceptable, thin-film, solid state rechargeable secondary battery system, other solid state systems need to be developed. The solid state battery systems of the present invention meet the requirements discussed hereinabove and provide gravimetric and volumetric energy densities of unparalleled performance.

35 Metal hydride negative electrode materials were originally classified as AB<sub>2</sub> based material or AB<sub>5</sub> (mischmetal) based materials. Modern metal hydride negative electrode materials are all multiphase multicomponent materials often referred to as Ovonic materials. These materials are discussed in detail in U.S. Patent Application No. 07/ 934,976 to Ovshinsky and Fetcenko, the contents of which are incorporated by reference.

5 The first hydrogen storage alloys to be investigated as battery electrode materials were TiNi and LaNi<sub>5</sub>. Many years were spent in studying these simple binary intermetallics because they were known to have the proper hydrogen bond strength for use in electrochemical applications. Despite extensive efforts, however, researchers found these intermetallics to be extremely unstable and of marginal electrochemical value due to a variety of problems such as slow discharge, oxidation, corrosion, poor kinetics, poor catalysis, and poor cycle life. The initial use of these simple alloys for battery applications reflect the traditional bias of battery developers toward the use of single element couples of crystalline materials such as NiCd, NaS, LiMS, ZnBr, NiFe, NiZn, and Pb-acid. In order to improve the electrochemical properties of the binary intermetallics while maintaining the hydrogen storage efficiency, early workers began modifying TiNi and LaNi<sub>5</sub> systems.

10 The modification of TiNi and LaNi<sub>5</sub> was initiated by Stanford R. Ovshinsky at Energy Conversion Devices (ECD) of Troy, Michigan. Upon a detailed investigation, Ovshinsky and his team at ECD showed that reliance on simple, relatively pure compounds was a major shortcoming of the prior art. Prior work had determined that catalytic action depends on surface reactions at sites of irregularities in the crystal structure. Relatively pure compounds were found to have a relatively low density of hydrogen storage sites, and the type of sites available occurred accidentally and were not designed into the bulk of the material. Thus, the efficiency of the storage of hydrogen and the subsequent release of hydrogen to form water was determined to be substantially less than that which would be possible if a greater number and variety of active sites were available. By engineering a disordered material having an ordered local environment, the entire bulk of the material can be provided with catalytically active hydrogen storage sites. Ovshinsky had previously found that the number of surface sites could be increased by making an amorphous film that resembled the surface of the desired relatively pure materials. See, Principles and Applications of Amorphicity, Structural Change, and Optical Information Encoding, 42 Journal De Physique at C4-1096 (October 1981).

25 Thus, rather than searching for material modifications that would yield ordered materials having a maximum number of accidentally occurring surface irregularities, Ovshinsky and his team at ECD began constructing "disordered" materials where the desired irregularities were synthetically engineered and tailor made. See, U.S. Patent No. 4,623,597, the disclosure of which is incorporated by reference. The term "disordered," as used herein corresponds to the meaning of the term as used in the literature, such as the following:

30 [Disordered material] can exist in several structural states. This structural factor constitutes a new variable with which the physical properties of the [material] ... can be controlled. Furthermore, structural disorder opens up the possibility of preparing in a metastable state new compositions and mixtures that far exceed the limits of thermodynamic equilibrium. Hence, we note the

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following as a further distinguishing feature. In many disordered [materials] ... it is possible to control the short-range order parameter and thereby achieve drastic changes in the physical properties of these materials, including forcing new coordination numbers for elements.... S. R. Ovshinsky, The Shape of Disorder, 32 Journal of Non-Crystalline Solids at 22 (1979).

The "short-range order" of disordered materials is explained further by Ovshinsky in The Chemical Basis of Amorphicity: Structure and Function, 26:8-9 Rev. Roum. Phys. at 893-903 (1981):

[S]hort-range order is not conserved .... Indeed, when crystalline symmetry is destroyed, it becomes impossible to retain the same short-range order. The reason for this is that the short-range order is controlled by the force fields of the electron orbitals. Therefore, the environment must be fundamentally different in corresponding crystalline and amorphous solids. In other words, it is the interaction of the local chemical bonds with their surrounding environment which determines the electrical, chemical, and physical properties of the material, and these can never be the same in amorphous materials as they are in crystalline materials... The orbital relationships that can exist in three-dimensional space in amorphous but not crystalline materials are the basis for new geometries, many of which are inherently anti-crystalline in nature. Distortion of bonds and displacement of atoms can be an adequate reason to cause amorphicity in single component materials. But to sufficiently understand the amorphicity, one must understand the three-dimensional relationships inherent in the amorphous state, for it is they which generate internal topology incompatible with the translational symmetry of the crystalline lattice .... What is important in the amorphous state is the fact that one can make an infinity of materials that do not have any crystalline counterparts, and that even the ones that do are similar primarily in chemical composition. The spatial and energetic relationships of these atoms can be entirely different in the amorphous and crystalline forms, even though their chemical elements can be the same....

Short-range, or local, order is elaborated on in U.S. Patent No. 4,520,039 to Ovshinsky, entitled Compositionally Varied Materials and Method for Synthesizing the Materials, the contents of which are incorporated by reference. This patent discusses how disordered materials do not require any periodic local order and how, by using Ovshinsky's techniques, spatial and orientational placement of similar or dissimilar atoms or groups of atoms is possible with such increased precision and control of the local configurations that it is possible to produce qualitatively new phenomena. In addition, this patent discusses that the atoms used

need not be restricted to "d band" or "f band" atoms, but can be any atom in which the controlled aspects of the interaction with the local environment plays a significant role physically, electrically, or chemically so as to affect the physical properties and hence the functions of the materials. These techniques result in means of synthesizing new materials which are disordered in several different senses simultaneously.

By forming metal hydride alloys from such disordered materials, Ovshinsky and his team were able to greatly increase the reversible hydrogen storage characteristics required for efficient and economical battery applications, and produce batteries having high density energy storage, efficient reversibility, high electrical efficiency, bulk hydrogen storage without structural change or poisoning, long cycle life, and deep discharge capability. These materials are discussed in detail in U.S. Patent No. 4,623,597, the contents of which are incorporated by reference.

The improved characteristics of these alloys result from tailoring the local chemical order and hence the local structural order by the incorporation of selected modifier elements into a host matrix. Disordered metal hydride alloys have a substantially increased density of catalytically active sites and storage sites compared to conventional ordered materials. These additional sites are responsible for improved efficiency of electrochemical charging/discharging and an increase in electrical energy storage capacity. The nature and number of storage sites can even be designed independently of the catalytically active sites. More specifically, these disordered multi-component alloys are thermodynamically tailored to allow storage of hydrogen atoms at a wide range of modulated bonding strengths within the range of reversibility suitable for use in secondary battery applications.

Based on these principles of disordered materials, described above, a family of extremely efficient electrochemical hydrogen storage materials were formulated. These are the Ti-V-Zr-Ni type active materials such as disclosed in U.S. Patent No. 4,551,400. The materials of the '400 Patent are generally multiphase materials, which may contain, but are not limited to, one or more phases of Ti-V-Zr-Ni material with C14 and C15 type crystal structures. Other Ti-V-Zr-Ni alloys may also be used for fabricating rechargeable hydrogen storage negative electrodes. One such family of materials are those described in U.S. Patent No. 4,728,586 ("the '586 Patent") to Venkatesan, Reichman, and Fetcenko for Enhanced Charge Retention Electrochemical Hydrogen Storage Alloys and an Enhanced Charge Retention Electrochemical Cell, the disclosure of which is incorporated by reference. The '586 Patent describes a specific sub-class of these Ti-V-Ni-Zr alloys comprising Ti, V, Zr, Ni, and a fifth component, Cr. The '586 patent, mentions the possibility of additives and modifiers beyond the Ti, V, Zr, Ni, and Cr components of the alloys, and generally discusses specific additives and modifiers, the amounts and interactions of these modifiers, and the particular benefits that could be expected from them.

The V-Ti-Zr-Ni family of alloys described in the '586 Patent has an inherently higher discharge rate capability than previously described alloys. This is the result of substantially higher surface areas at the metal/electrolyte interface for electrodes made from the V-Ti-Zr-Ni materials. The surface roughness factor (total surface area divided by geometric surface area) of the V-Ti-Zr-Ni is about 10,000. This value indicates a very high surface area. The validity of this value is supported by the inherently high rate capability of these materials.

The characteristic surface roughness of the metal electrolyte interface is a result of the disordered nature of the material. Since all of the constituent elements, as well as many alloys and phases of them, are present throughout the metal, they are also represented at the surfaces and at cracks which form in the metal/electrolyte interface. Thus, the characteristic surface roughness is descriptive of the interaction of the physical and chemical properties of the host metals as well as of the alloys and crystallographic phases of the alloys, in an alkaline environment. The microscopic chemical, physical, and crystallographic parameters of the individual phases within the hydrogen storage alloy material are believed to be important in determining its macroscopic electrochemical characteristics.

In addition to the physical nature of its roughened surface, it has been observed that V-Ti-Zr-Ni alloys tend to reach a steady state surface condition and particle size. This steady state surface condition is characterized by a relatively high concentration of metallic nickel. These observations are consistent with a relatively high rate of removal through precipitation of the oxides of titanium and zirconium from the surface and a much lower rate of nickel solubilization. The resultant surface seems to have a higher concentration of nickel than would be expected from the bulk composition of the negative hydrogen storage electrode. Nickel in the metallic state is electrically conductive and catalytic, imparting these properties to the surface. As a result, the surface of the negative hydrogen storage electrode is more catalytic and conductive than if the surface contained a higher concentration of insulating oxides.

The surface of the negative electrode, which has a conductive and catalytic component -- the metallic nickel -- appears to interact with chromium alloys in catalyzing various hydride and dehydride reaction steps. To a large extent, many electrode processes, including competing electrode processes, are controlled by the presence of chromium in the hydrogen storage alloy material, as disclosed in the '586 Patent.

Simply stated, in the AB5 alloys, like the V-Ti-Zr-Ni alloys, as the degree of modification increases, the role of the initially ordered base alloy is of minor importance compared to the properties and disorder attributable to the particular modifiers. In addition, analysis of the current multiple component AB5 alloys indicates that current AB5 alloy systems are modified following the guidelines established for V-Ti-Zr-Ni based systems. Thus, highly modified AB5 alloys are identical to V-Ti-Zr-Ni based alloys in that both are disordered materials that are characterized by multiple-components and multiple phases and therefore no

longer exists any significant distinction between multicomponent, multiphase V-Ti-Zr-Ni based alloys and AB5 alloys.

In rechargeable alkaline cells using a nickel hydroxide positive electrode, the nickel hydroxide changes back and forth between  $\text{Ni(OH)}_2$  and  $\text{NiOOH}$  as the cell is charged and discharged. Bode, et al., described the relationship between the different structural phases that occur in such an electrode as presented in 11 Electrochem. Acta 1079 (1966). These structures represent plates of crystallized nickel hydroxide positive electrode material held in position by a variety of ionic species. In unmodified nickel hydroxide electrode materials cycling occurs from the beta-(II) phase and the beta-(III) phase structures because they are the most stable. During such cycling one electron is transferred. The theoretical specific capacity of the nickel hydroxide active material based on this reaction is 289 mAh/g.

In contrast to beta phase cycling, alpha-gamma phase cycling appears to involve the transfer of at least 1.5 electrons. (See, for example, Oliva et al., 8 J. Power Sources 229 (1982)). Multiple electron transfer materials having increased cell capacity are described in detail in U.S. Patent Application No. 08/027,973 (the contents of which are incorporated by reference). These materials exhibit a 1.7 electron oxidation with a nickel valence of 3.67 according to equation.

#### SUMMARY OF THE INVENTION

The present application is a solid state battery comprising a substrate; at least one multilayered electrochemical cell deposited onto the substrate, each layer of the multilayered electrochemical cell comprising: a layer of negative electrode material capable of electrochemically adsorbing and desorbing ions during charge and discharge; a layer of positive electrode material capable of electrochemically desorbing and adsorbing ions during charge and discharge; and a layer of insulating/conducting material disposed between the layer of positive electrode material and the layer of negative electrode material, where the layer of insulating/conducting material is electrically insulating and capable of readily conducting or transporting ions from the layer positive electrode material to the layer of negative electrode material while the battery is charging and from the layer of negative electrode material to the layer of positive electrode material while the battery is discharging; and an electrically conductive layer deposited a top the last of the at least one multilayered electrochemical cells, the electrically conductive layer providing one battery terminal.

In a preferred embodiment, the positive electrode layer includes at least nickel hydroxide and the negative electrode material includes at least a metal hydride, which may be a disordered, multiphase, multicomponent metal hydride material. The solid state proton conducting material includes at least a hydrogenated electrical insulator material, which may be a hydrogenated silicon nitride material. The hydrogenated silicon nitride material preferably has an atomic ratio of between 20 and 50 atomic percent hydrogen, between 20 and 40 atomic

percent silicon and between 20 and 50 atomic percent nitrogen. Preferably the substrate material is formed from an electrically conductive material and acts as one of the electrical terminal of the battery. However, the substrate material may be electrically insulating with an electrically conductive material deposited on it. The deposited electrically conductive material acts as the one of the battery terminals. When the battery includes more than one multi-layered cell, current collector material layers are deposited between the positive electrode of one cell and the negative electrode of the adjacent cell. Typically, the electrically conductive battery terminals and the current collector material layers are formed from non-reactive metals such as nickel.

A second embodiment of the present invention includes a solid state electrolyte. The solid state electrolyte is electrically non-conductive while at the same time being readily conductive to protons. The solid state electrolyte preferably is a hydrogenated electrically insulating material, such as a hydrogenated silicon nitride material. The hydrogenated silicon nitride solid state electrolyte of the present invention preferably includes, by atomic percentage between 20 and 50 percent hydrogen, between 20 and 40 percent silicon, and between 20 and 50 percent nitrogen.

#### BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a cross-sectional depiction of a first embodiment of the solid state battery of the instant invention specifically illustrating the individual layers thereof;

Figure 2 is a cross-sectional depiction of a second embodiment of the solid state battery of the instant invention specifically illustrating the individual layers thereof, including plural electrochemical cells and current collectors therebetween.

#### DETAILED DESCRIPTION OF THE INVENTION

Figure 1 is a cross-sectional depiction of a thin-film solid state battery of the present invention. Specifically, reference numeral 1 is the substrate of the thin-film battery. The substrate provides support for the battery and may also serve as the bottom electrical terminal of the battery. Substrate 1 may be formed from an electrically conductive metal such as aluminum, nickel, copper or stainless steel, or it may be formed from a light weight, electrically insulating polymer or ceramic material. If the substrate 1 is formed of an electrically insulating material, then an electrically conductive bottom battery terminal layer 2 is deposited onto the substrate. The material used to form the battery terminal layer 2 may be an electrically conductive metal such as aluminum, nickel or copper, or may even be an electrically conductive ceramic or oxide material. For maximum weight savings, the substrate 1 plus any battery terminal layer 2 should be only as thick as needed to perform their support and conduction functions. Any additional thickness will only increase the "dead weight" of the battery. Typically the total thickness of the substrate 1 plus the battery terminal layer 2 will not be greater than about 200 microns and preferably not greater than about 50 to 100 microns. The

battery terminal layer 2 is preferably between 1 and 5 microns thick. Deposited on top of the substrate 1 and battery terminal layer 2 is at least one multi-layered electrochemical cell. Each electrochemical cell includes a thin-film negative electrode layer 3, a thin-film positive electrode layer 5 and a thin-film solid electrolyte proton conductive layer 4.

5 The thin-film negative electrode layer 3 is typically between about 1 and 15 microns thick and is formed from a material which electrochemically adsorbs and desorbs ions such as ionic hydrogen during charging and discharging thereof, respectively. Typically the layer is formed from electrochemical hydrogen storage materials such as metal hydride materials. These metal hydride material may be any of those already known any used in liquid electrolyte 10 nickel-metal hydride batteries. These materials may be  $AB_2$  or  $AB_3$  type metal hydride materials. They may be amorphous, polycrystalline, microcrystalline, nanocrystalline, single crystal or multi-structural materials. They may include only a single compositional phase or may include multiple compositional phases. An extensive review of the known metal hydride materials useful in electrochemical cells is given in U.S. Patent No. 5,096,667, the disclosure 15 of which is incorporated herein by reference.

In addition to the known metal hydride materials, new metal hydride systems can be developed to take advantage of the environmental differences between an alkaline liquid electrolyte system and the new thin-film solid electrolyte systems. For example, in a liquid electrolyte system, there is generally a problem with corrosion of the electrode due to the 20 caustic nature of the alkaline electrolyte. Therefore, elements which provide corrosion resistance must be added to the negative electrode material to mitigate corrosion damage. In the solid electrolyte system of the present invention, no such corrosion problems will occur due to the absence of caustic liquids and as such, no corrosion inhibitor materials will need to be added to the negative electrode.

25 Alternatively, for lithium ion systems, the negative electrode layer can be formed from a material such as lithium nickelate ( $LiNiO_2$ ), lithium cobaltate or ( $LiCoO_2$ ) lithium manganate ( $LiMnO_2$ ).

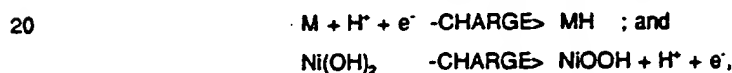
The positive electrode layer 5 is typically between 5 and 20 microns thick and is formed from a material which electrochemically desorbs and adsorbs ions such as ionic hydrogen 30 during charging and discharging thereof, respectively. Typically the layer is formed from a transition metal hydroxide such as nickel hydroxide material. The nickel hydroxide material can be any of those material known in the prior art for use in rechargeable battery systems. They may also be advanced active materials like the locally ordered, disordered, high capacity, long cycle life positive electrode material disclosed in U.S. Patent Application Serial No.s 7/975,031 35 filed November 12, 1992 and 8/027,973 filed March 8, 1993, the disclosures of which are incorporated herein by reference. These materials include a solid solution nickel hydroxide electrode material having a multiphase structure and at least one compositional modifier to



promote said multiphase structure. The multiphase structure comprises at least one polycrystalline  $\gamma$ -phase including a polycrystalline  $\gamma$ -phase unit cell comprising spacedly disposed plates with at least one ion incorporated around the plates, the plates having a range of stable intersheet distances corresponding to a 2<sup>+</sup> oxidation state and a 3.5<sup>+</sup> or greater, oxidation state. The compositional modifier is a metal, a metallic oxide, a metallic oxide alloy, a metal hydride, and/or a metal hydride alloy. Preferably the compositional modifier is chosen from the group consisting of Al, Bi, Co, Cr, Cu, Fe, In, LaH<sub>3</sub>, Mn, Ru, Sb, Sn, TiH<sub>2</sub>, TiO, Zn and mixtures thereof. More preferably, at least three of these compositional modifiers are used. The at least one chemical modifier incorporated is preferably chosen from the group consisting of Al, Ba, Ca, Co, Cr, Cu, F, Fe, K, Li, Mg, Mn, Na, Sr, and Zn.

Also, in the case of lithium systems, lithium intercalated carbon can be used as the positive electrode layer 5.

Between the negative electrode layer 3 and the positive electrode layer 5, is deposited a thin-film solid state electrolyte layer 4. This layer is typically between about 0.5 and 2 microns thick, but may be as thin as 1000 Angstroms if the layer onto which it is deposited has a low degree of surface roughness. The type of ionic conductivity required of the solid electrolyte is dependent on the electrochemical reactions involved in the cell. Since the charging cycle electrode reactions of the instant rechargeable protonic battery are:



the solid state electrolyte layer 4 which separates the positive electrode layer 5 and the negative electrode layer 3 must be a proton conductor. That is, the solid electrolyte material must be capable of readily conducting or transporting protons from the positive electrode layer 5 to the negative electrode layer 3 while the battery is charging and from the negative electrode layer 3 to the positive electrode layer 5 while the battery is discharging. The solid electrolyte layer 4 must also be electrically insulating so that the battery electrodes do not short. That is, the electrolyte also acts as the electrode separator. The present inventors have found that a hydrogenated electrical insulator has all of the characteristics required. Typically this is a hydrogenated silicon nitride material, but hydrogenated silicon oxide or hydrogenated silicon oxynitride may also be used. Preferably the hydrogenated silicon nitride material has a composition, in atomic percent, of between about 20% and about 50% Hydrogen, between about 20% and about 40% silicon and about 20% to about 50 %. The ratio of silicon to nitrogen is generally between about 2:1 and about 1:2, but may be varied outside this range if specifically advantageous under the circumstances.

Alternatively, for the lithium systems, the charging electrode reactions are:



15



therefore, in the lithium systems, a lithium conductor is needed. Solid lithium conductors useful as the ionic conductor layer 4 are lithiated silicon nitride ( $\text{Li}_x\text{SiN}_2$ ), lithium phosphate ( $\text{LiPO}_4$ ), lithium titanium phosphate ( $\text{LiTiPO}_4$ ) and lithium phosphonitride ( $\text{LiPO}_{1-x}\text{N}_x$  where  $0 < x < 1$ ).

5 A top battery terminal layer 6 is deposited on top of the positive electrode layer 5. The battery terminal layer 6 is typically between 1 and 5 microns thick and is formed from an electrically conductive material such as a metal or an electrically conductive ceramic or oxide. Specifically, aluminum, copper or nickel may be used.

Turning now to Figure 2 there is depicted therein a solid state battery of the instant invention containing multiple stacked electrochemical cells. The reference numeral of the layers of this battery correspond to those of the battery depicted in Figure 1. Additionally, because this battery includes more than one electrochemical cell, a layer of current collecting material 7 is deposited between positive electrode layer 5 of one cell and the negative electrode layer 3 of the adjacent cell. This layer is formed of an electrically conductive material and is typically between 1000 angstroms and 0.5 microns thick. Preferably this layer is formed from a metal such as aluminum, copper or nickel and is resistant to the conduction of protons.

#### EXAMPLE 1

A one square meter multiple cell thin-film solid state battery of the type depicted in Figure 2 having 10 cells will serve as an example of the efficacy of the present design. Each cell contains a positive electrode layer 5 which is formed from conventional nickel hydroxide and is about 10 microns thick. Each cell also contains a negative electrode layer 3 of metal hydride material and is about 4 microns thick. Finally each cell contains a solid state electrolyte layer 4 formed from hydrogenated silicon nitride material and is about 2 microns thick. Between the cells are current collector layers 7 which are formed of aluminum and are about 0.5 microns thick. The cells are deposited onto an aluminum substrate 1 which also serves as the bottom battery terminal 2. The substrate 1 is about 100 microns thick. On top of the positive electrode layer 5 of the final cell is deposited a top battery terminal layer 6 which is formed of aluminum and is about 5 microns thick.

This battery would have a Specific Capacity calculated as follows:

- 1) Basis 1 m<sup>2</sup>, 1 e<sup>-</sup> transfer; 10 positive electrode layers formed from  $\text{Ni}(\text{OH})_2$
- 2) Density of  $\text{Ni}(\text{OH})_2$  = 3.95 g/cm<sup>3</sup>
- 3) Total volume of 10  $\text{Ni}(\text{OH})_2$  layers =  $10 \times (1\text{m}) \times (1\text{m}) \times (10 \times 10^{-6}\text{m}) = 1 \times 10^{-4} \text{ m}^3$  or 100 cm<sup>3</sup>
- 4) Total weight of 10  $\text{Ni}(\text{OH})_2$  layers =  $(3.95 \text{ g/cm}^3) \times (100 \text{ cm}^3) = 395 \text{ g Ni}(\text{OH})_2$
- 5) Charge capacity of  $\text{Ni}(\text{OH})_2$  = 289 mAh/g
- 6) Total capacity of 10  $\text{Ni}(\text{OH})_2$  layers =  $(289 \text{ mAh/g}) \times (395 \text{ g}) = 114115 \text{ mAh} =$

114.1 Ah

- 7) Charge capacity of metal hydride material = 400 mAh/g
- 8) Weight of metal hydride needed to equal 114.1 Ah =  $(114.1 \text{ ah}) \cdot (1\text{g}/.400 \text{ Ah})$   
= 285 g
- 9) Volume of substrate =  $(1\text{m}) \cdot (1\text{m}) \cdot (100 \times 10^{-6}\text{m}) = 1 \times 10^{-4}\text{m}^3 = 100 \text{ cm}^3$
- 10) Weight of substrate =  $(2.7 \text{ g/cm}^3) \cdot (100 \text{ cm}^3) = 270 \text{ g}$
- 11) Total volume of 10 hydrogenated silicon nitride layers =  $10 \cdot (1\text{m}) \cdot (1\text{m}) \cdot (2 \times 10^{-6}\text{m}) = 2 \times 10^{-5}\text{m}^3 = 20 \text{ cm}^3$
- 12) Total weight of 10 hydrogenated silicon nitride layers =  $(1.7 \text{ g/cm}^3) \cdot (20 \text{ cm}^3)$   
= 34 g
- 13) Total volume of 9 current collector layers =  $9 \cdot (1\text{m}) \cdot (1\text{m}) \cdot (0.5 \times 10^{-6}\text{m}) = 4.5 \times 10^{-6}\text{m}^3 = 4.5 \text{ cm}^3$
- 14) Total weight of 9 current collector layers =  $(2.7 \text{ g/cm}^3) \cdot (4.5 \text{ cm}^3) = 12.15 \text{ g}$
- 15) Volume of top battery terminal =  $(1\text{m}) \cdot (1\text{m}) \cdot (5 \times 10^{-6}\text{m}) = 5 \times 10^{-6}\text{m}^3 = 5 \text{ cm}^3$
- 16) Weight of top battery terminal =  $(2.7 \text{ g/cm}^3) \cdot (5 \text{ cm}^3) = 13.5 \text{ g}$
- 17) Total battery weight =  $(395 \text{ g}) + (285 \text{ g}) + (270 \text{ g}) + (34 \text{ g}) + (12.15 \text{ g}) + (13.5 \text{ g}) =$   
 $1009.65 \text{ g} = 1.01 \text{ Kg}$
- 18) Specific capacity is  $(114.155 \text{ Ah}) / (1.00965 \text{ Kg}) = 113.1 \text{ Ah/Kg}$
- 19) Energy density is  $(1.4 \text{ V}) \cdot (113.1 \text{ Ah/Kg}) = 158.34 \text{ Wh/Kg}$
- 20) Volume of battery =  $(1\text{m}) \cdot (1\text{m}) \cdot (250 \times 10^{-6}\text{m}) = 2.5 \times 10^{-4}\text{m}^3 = 0.25 \text{ l}$
- 21) Volumetric energy density is  $(114.155 \text{ Ah}) \cdot (1.4 \text{ V}) / (0.25 \text{ l}) = 639.3 \text{ Wh/l}$

## EXAMPLE 2

Another example of the solid state battery having the same structure and dimensions as that in Example 1, but using advanced nickel hydroxide active materials and assuming about 1.7 electron transfer give a specific capacity as calculated below.

- 1) Basis  $1 \text{ m}^2$ ,  $1.7 \text{ e}^-$  transfer; 10 positive electrode layers formed from advanced  $\text{Ni}(\text{OH})_2$  material
- 2) Density of  $\text{Ni}(\text{OH})_2 = 3.95 \text{ g/cm}^3$
- 3) Total volume of 10  $\text{Ni}(\text{OH})_2$  layers =  $10 \cdot (1\text{m}) \cdot (1\text{m}) \cdot (10 \times 10^{-6}\text{m}) = 1 \times 10^{-4} \text{ m}^3$   
or  $100 \text{ cm}^3$
- 4) Total weight of 10  $\text{Ni}(\text{OH})_2$  layers =  $(3.95 \text{ g/cm}^3) \cdot (100 \text{ cm}^3) = 395 \text{ g Ni}(\text{OH})_2$
- 5) Charge capacity of  $\text{Ni}(\text{OH})_2 = 483 \text{ mAh/g}$
- 6) Total capacity of 10  $\text{Ni}(\text{OH})_2$  layers =  $(483 \text{ mAh/g}) \cdot (395 \text{ g}) = 190785 \text{ mAh} =$   
 $190.8 \text{ Ah}$
- 7) Charge capacity of metal hydride material = 400 mAh/g
- 8) Weight of metal hydride needed to equal 190.8 Ah =  $(190.8 \text{ ah}) \cdot (1\text{g}/.400 \text{ Ah})$   
= 477 g

17

- 9) Volume of substrate =  $(1\text{m}) \cdot (1\text{m}) \cdot (100 \times 10^{-6}\text{m}) = 1 \times 10^{-4}\text{m}^3 = 100 \text{ cm}^3$
- 10) Weight of substrate =  $(2.7 \text{ g/cm}^3) \cdot (100 \text{ cm}^3) = 270 \text{ g}$
- 11) Total volume of 10 hydrogenated silicon nitride layers =  $10 \cdot (1\text{m}) \cdot (1\text{m}) \cdot (2 \times 10^{-6}\text{m}) = 2 \times 10^{-5}\text{m}^3 = 20 \text{ cm}^3$
- 5 12) Total weight of 10 hydrogenated silicon nitride layers =  $(1.7 \text{ g/cm}^3) \cdot (20 \text{ cm}^3) = 34 \text{ g}$
- 13) Total volume of 9 current collector layers =  $9 \cdot (1\text{m}) \cdot (1\text{m}) \cdot (0.5 \times 10^{-6}\text{m}) = 4.5 \times 10^{-6}\text{m}^3 = 4.5 \text{ cm}^3$
- 14) Total weight of 9 current collector layers =  $(2.7 \text{ g/cm}^3) \cdot (4.5 \text{ cm}^3) = 12.15 \text{ g}$
- 10 15) Volume of top battery terminal =  $(1\text{m}) \cdot (1\text{m}) \cdot (5 \times 10^{-6}\text{m}) = 5 \times 10^{-6}\text{m}^3 = 5 \text{ cm}^3$
- 16) Weight of top battery terminal =  $(2.7 \text{ g/cm}^3) \cdot (5 \text{ cm}^3) = 13.5 \text{ g}$
- 17) Total battery weight =  $(395 \text{ g}) + (477 \text{ g}) + (270 \text{ g}) + (34 \text{ g}) + (12.15 \text{ g}) + (13.5 \text{ g}) = 1201.65 \text{ g} = 1.20165 \text{ Kg}$
- 18) Specific capacity is  $(190.785 \text{ Ah}) / (1.20165 \text{ Kg}) = 158.8 \text{ Ah/Kg}$
- 15 19) Gravimetric energy density is  $(1.4 \text{ V}) \cdot (158.8 \text{ Ah/Kg}) = 222.32 \text{ Wh/Kg}$
- 20) Volume of battery =  $(1\text{m}) \cdot (1\text{m}) \cdot (250 \times 10^{-6}\text{m}) = 2.5 \times 10^{-4}\text{m}^3 = 0.25 \text{ l}$
- 21) Volumetric energy density is  $(190.785 \text{ Ah}) \cdot (1.4 \text{ V}) / (0.25 \text{ l}) = 1068.4 \text{ Wh/l}$

## EXAMPLE 3

20 Next, a battery similar to that disclosed in Example 1 except that the protonic system was substituted by a lithium system is presented. Each of the 10 cells contains a positive electrode layer 5 which is formed from lithium nickelate ( $\text{LiNiO}_2$ ) and is about 10 microns thick. Each cell also contains a negative electrode layer 3 of carbon material and is about 4 microns thick. Finally each cell contains a solid state electrolyte layer 4 formed from lithiated silicon nitride material and is about 2 microns thick. Between the cells are current collector layers 7

25 which are formed of aluminum and are about 0.5 microns thick. The cells are deposited onto an aluminum substrate 1 which also serves as the bottom battery terminal 2. The substrate 1 is about 100 microns thick. On top of the positive electrode layer 5 of the final cell is deposited a top battery terminal layer 6 which is formed of aluminum and is about 5 microns thick.

30 This battery would have a Specific Capacity calculated as follows:

- 1) Basis  $1 \text{ m}^2$ ,  $1 \text{ e}^-$  transfer; 10 positive electrode layers formed from  $\text{LiNiO}_2$
- 2) Density of  $\text{LiNiO}_2 = 4.78 \text{ g/cm}^3$
- 3) Total volume of 10  $\text{LiNiO}_2$  layers =  $10 \cdot (1\text{m}) \cdot (1\text{m}) \cdot (10 \times 10^{-6}\text{m}) = 1 \times 10^{-4} \text{ m}^3$  or  $100 \text{ cm}^3$
- 35 4) Total weight of 10  $\text{LiNiO}_2$  layers =  $(4.78 \text{ g/cm}^3) \cdot (100 \text{ cm}^3) = 478 \text{ g LiNiO}_2$
- 5) Charge capacity of  $\text{LiNiO}_2 = 275 \text{ mAh/g}$
- 6) Total capacity of 10  $\text{LiNiO}_2$  layers =  $(275 \text{ mAh/g}) \cdot (478 \text{ g}) = 131450 \text{ mAh} =$

131.5 Ah

- 7) Charge capacity of carbon intercalation material = 370 mAh/g
- 8) Weight of carbon needed to equal 131.5 Ah =  $(131.5 \text{ Ah}) \cdot (1 \text{ g} / 37 \text{ Ah}) = 355.3 \text{ g}$
- 5 9) Volume of substrate =  $(1 \text{ m}) \cdot (1 \text{ m}) \cdot (100 \times 10^{-6} \text{ m}) = 1 \times 10^{-4} \text{ m}^3 = 100 \text{ cm}^3$
- 10 10) Weight of substrate =  $(2.7 \text{ g/cm}^3) \cdot (100 \text{ cm}^3) = 270 \text{ g}$
- 11) Total volume of 10 lithiated silicon nitride layers =  $10 \cdot (1 \text{ m}) \cdot (1 \text{ m}) \cdot (2 \times 10^{-6}) = 2 \times 10^{-4} \text{ m}^3 = 20 \text{ cm}^3$
- 12) Total weight of 10 lithiated silicon nitride layers =  $(1.7 \text{ g/cm}^3) \cdot (20 \text{ cm}^3) = 34 \text{ g}$
- 10 13) Total volume of 9 current collector layers =  $9 \cdot (1 \text{ m}) \cdot (1 \text{ m}) \cdot (0.5 \times 10^{-6} \text{ m}) = 4.5 \times 10^{-4} \text{ m}^3 = 4.5 \text{ cm}^3$
- 14) Total weight of 9 current collector layers =  $(2.7 \text{ g/cm}^3) \cdot (4.5 \text{ cm}^3) = 12.15 \text{ g}$
- 15) Volume of top battery terminal =  $(1 \text{ m}) \cdot (1 \text{ m}) \cdot (5 \times 10^{-6} \text{ m}) = 5 \times 10^{-4} \text{ m}^3 = 5 \text{ cm}^3$
- 16) Weight of top battery terminal =  $(2.7 \text{ g/cm}^3) \cdot (5 \text{ cm}^3) = 13.5 \text{ g}$
- 15 17) Total battery weight =  $(478 \text{ g}) + (355.3 \text{ g}) + (270 \text{ g}) + (34 \text{ g}) + (12.15 \text{ g}) + (13.5 \text{ g}) = 1162.95 \text{ g} = 1.16 \text{ Kg}$
- 18) Specific capacity is  $(131.450 \text{ Ah}) / (1.16 \text{ Kg}) = 113.0 \text{ Ah/Kg}$
- 19) Energy density is  $(3.8 \text{ V}) \cdot (113.0 \text{ Ah/Kg}) = 429.5 \text{ Wh/Kg}$
- 20 20) Volume of battery =  $(1 \text{ m}) \cdot (1 \text{ m}) \cdot (250 \times 10^{-6} \text{ m}) = 2.5 \times 10^{-4} \text{ m}^3 = 0.25 \text{ l}$
- 21) Volumetric energy density is  $(131.450 \text{ Ah}) \cdot (3.8 \text{ V}) / (0.25 \text{ l}) = 1998.04 \text{ Wh/l}$

Therefore, it can clearly be seen that the solid state batteries of the present invention show tremendous promise for commercial, industrial and consumer uses. Particularly, with regard to the gravimetric and volumetric energy densities shown above, application of these batteries to electric vehicle would be highly advantageous.

- 25 It is to be understood that the disclosure set forth herein is presented in the form of detailed embodiments described for the purpose of making a full and complete disclosure of the present invention, and that such details are not to be interpreted as limiting the true scope of this invention as set forth and defined in the appended claims.

We claim:

1. A solid state battery comprising:  
a substrate;

5 at least one multilayered electrochemical cell deposited onto said substrate, each layer of said multilayered electrochemical cell comprising:  
a layer of negative electrode material capable of electrochemically adsorbing and desorbing ions during charge and discharge;  
a layer of positive electrode material capable of electrochemically desorbing and adsorbing ions during charge and discharge; and  
10 a layer of insulating/conducting material disposed between said layer of positive electrode material and said layer of negative electrode material, where said layer of insulating/conducting material is electrically insulating and capable of readily conducting or transporting ions from said layer positive electrode material to said layer of negative electrode material while said battery is charging and from said layer of negative electrode material to said layer of positive electrode material while said battery is discharging; and  
15 an electrically conductive layer deposited a top the last of said at least one multilayered electrochemical cells, said electrically conductive layer providing one battery terminal.

2. The solid state battery of claim 1, wherein said layer of negative electrode material and said layer of positive electrode material are capable of electrochemically desorbing and adsorbing protons during charge and discharge; and said layer of insulating/conducting material conducts or transports protons between said layer of positive electrode material and said layer of negative electrode material.

3. The solid state battery of claim 1, wherein said layer of negative electrode material, said layer of positive electrode material, and said layer of insulating/conducting material are all thin film materials.

4. The solid state battery of claim 2, wherein said layer of negative electrode material, said layer of positive electrode material, and said layer of insulating/conducting material are all thin film materials.

5. The solid state battery of claim 3, wherein said layer of positive electrode material comprises a material chosen from the group consisting of a transition metal hydroxide and  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ , and  $\text{LiMnO}_2$ .

6. The solid state battery of claim 4, wherein said layer of positive electrode material includes at least a transition metal hydroxide.

7. The solid state battery of claim 5, wherein said transition metal hydroxide is a

nickel hydroxide material which provides approximately one electron transfer.

8. The solid state battery of claim 6, wherein said transition metal hydroxide is a nickel hydroxide material which provides approximately one electron transfer.

5 9. The solid state battery of claim 5, wherein said nickel hydroxide material provides approximately 1.7 electron transfer.

10. The solid state battery of claim 6, wherein said nickel hydroxide material provides approximately 1.7 electron transfer.

11. The solid state battery of claim 3, wherein said layer of negative electrode material includes hydrogen-lithium storage compounds.

10 12. The solid state battery of claim 3, wherein said layer of negative electrode material is chosen from the group consisting of a metal hydride material and a carbon material that intercalates lithium.

13. The solid state battery of claim 12, wherein said layer of negative electrode material includes a metal hydride material.

15 14. The solid state battery of claim 12, wherein said layer of negative electrode material is disordered.

15. The solid state battery of claim 1, wherein said layer of negative electrode material is disordered.

20 16. The solid state battery of claim 1, wherein said layer of negative electrode material is a single phase or multiphase polycrystalline material.

17. The solid state battery of claim 16, wherein said layer of negative electrode material is a multiphase polycrystalline material.

18. The solid state battery of claim 1, wherein said layer of insulating/conducting material includes is a lithiated electrically insulating material.

25 19. The solid state battery of claim 2, wherein said insulating/conducting material includes a hydrogenated electrically insulating material.

20. The solid state battery of claim 2, wherein said insulating/conducting material includes a hydrogenated silicon nitride material.

30 21. The solid state battery of claim 2, wherein said insulating/conducting material is a hydrogenated silicon nitride film comprising: 20 to 50 atomic % hydrogen, 20 to 40 atomic % silicon, and 20 to 50 atomic % nitrogen.

22. The solid state battery of claim 3, wherein said substrate is electrically conductive and acts as a second electrical terminal of said battery.

35 23. The solid state battery of claim 4, wherein said substrate is electrically conductive and acts as a second electrical terminal of said battery.

24. The solid state battery of claim 3, wherein

said substrate is electrically insulative and  
an electrically conductive material layer is deposited onto said substrate, said electrically conductive material layer acting as a second battery terminal.

5        25.     The solid state battery of claim 4, wherein  
said substrate material is electrically insulative and  
an electrically conductive material layer is deposited onto said substrate, said electrically conductive material layer acting as a second battery terminal.

10       26.     The solid state battery of claim 1, comprising:  
more than one of said multilayered electrochemical cells and  
further comprises:  
current collector material layers deposited between said layer of positive electrode material of one multilayered electrochemical cell and said layer of negative electrode material of an adjacent multilayered electrochemical cell.

15       27.     The solid state battery of claim 2, comprising:  
more than one of said multilayered electrochemical cells and  
further comprises:  
current collector material layers deposited between said layer of positive electrode material of one multilayered electrochemical cell and said layer of negative electrode material of an adjacent multilayered electrochemical cell.

20       28.     The solid state battery of claim 24, wherein said electrically conductive material layer includes nickel.

29.     The solid state battery of claim 25, wherein said electrically conductive material includes nickel.

25       30.     A solid electrolyte, said solid electrolyte characterized by being electrically non-conductive while at the same time being readily conductive to protons.

31.     The solid electrolyte of claim 30, wherein said electrolyte is formed from a hydrogenated electrically insulative material.

32.     The solid electrolyte of claim 31, wherein said hydrogenated electrically insulative material is a hydrogenated silicon nitride material.

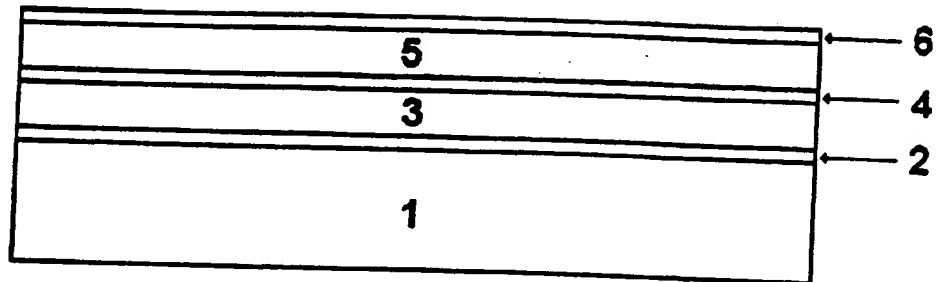
30       33.     The solid electrolyte of claim 32, wherein said hydrogenated silicon nitride material includes, by atomic percentage, between 20% and 50% hydrogen, between 20% and 40% silicon and between 20% and 50% nitrogen.

35       34.     The solid state battery of claim 1, wherein  
said negative electrode material comprises at least one component chosen  
from the group consisting of a metal hydride and carbon material that intercalates lithium;  
said positive electrode material comprises at least one component chosen from

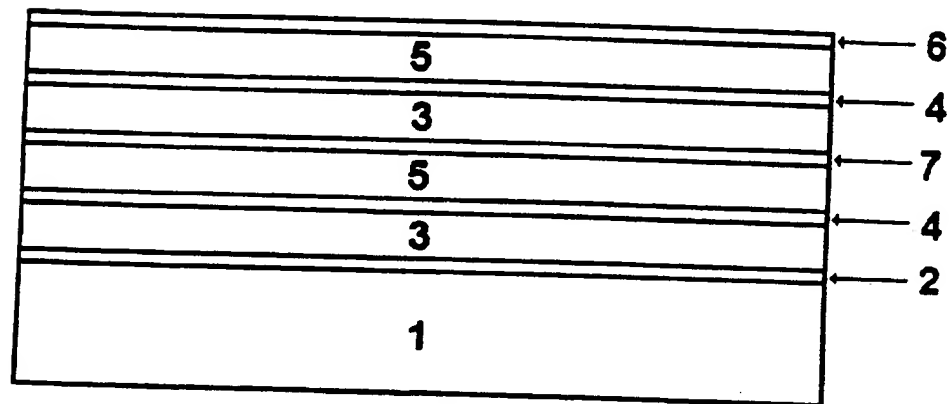


the group consisting of  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ , and  $\text{LiMnO}_2$ ; and  
said insulating/conducting material comprises at least one component chosen  
from the group consisting of  $\text{LiPO}_4$ ,  $\text{LiTiO}_4$ ,  $\text{LiPO}_{4-x}\text{N}_x$  where  $x = 0$  to  $1$ , and  $\text{Li}_6\text{SiN}_4$ .

1/1



**Fig. 1**



**Fig. 2**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/12297

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 6/18

US CL :429/191

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/191, 59, 152, 162, 178; 252/62.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, JPO search terms: electrolyte#, silicon nitride, lithium phosphate, lithium titanium phosphate, lithium phosphonitride

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,404,268 (IMAI ET AL.) 13 SEPTEMBER 1983 see the Abstract, Figure 1 and col. 2, lines 42-53.	1, 3, 11, 22
X	US, A, 4,810,599 (KONDO ET AL.) 7 MARCH 1989 see Figures 1,2 along with col. 3, line 22-col. 4, line 2.	1, 3, 11, 18, 22
X, P	US, A, 5,278,004 (PLICHTA ET AL.) 11 JANUARY 1994 see Figure 3 and col. 2, lines 32-62.	1, 3, 5, 11, 15, 18, 22
X, P	US, A, 5,264,305 (CHARKEY) 23 NOVEMBER 1993 see Fig 1 and col. 2, line 34-col. 4, line 53.	1

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier documents published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

18 JANUARY 1995

Date of mailing of the international search report

09 FEB 1995

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/12297

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,985,317 (ADACHI ET AL.) 15 JANUARY 1991	

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